HYDROGENATION OF COAL TAR AND COAL TAR OILS

BY

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ARMOUR INSTITUTE OF TECHNOLOGY

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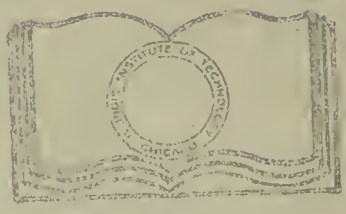

THE HYDROGENATION OF COAL TAR AND COAL TAR OILS

A THESIS

PRESENTED BY

ROBERT S. MELICHAR

TO THE

PRESIDENT AND FACULTY

OF

ARMOUR INSTITUTE OF TECHNOLOGY

FOR THE DEGREE OF

BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

MAY 29, 1919

APPROVED

A. M. McCormack
Professor of Chemical Engineering

H. M. Raymond
Dean of Engineering Studies

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INTRODUCTION.

Three problems present themselves to the tar distiller today. These are:-

In distilling tar for its products, fifty to seventy per cent of the tar is obtained as pitch. The outlook for pitch is exceedingly problematical. There is a possible outlet in the fuel field but competition here is too great. The production of tar has increased 100% in the last few years.

Tar oils which are liquid at ordinary temperatures are in much greater demand than tar oils which solidify at ordinary temperatures. The latter oils contain naphthalene which is the main constituent that causes them to solidify.

There is practically no demand for naphthalene. During the war, a considerable amount of it was used by the Ordinance Department of the U.S. Government. An outlet is therefore sought for the naphthalene which constitutes 5 to 7% of the tar.

By passing hydrogen through the tar

during distillation, it was thought that a larger production of oil could be obtained per gallon of tar. The idea being that the hot gas would be capable of absorbing the products of distillation and thus carry more of them over.

It was also thought that by passing the hydrogen through the tar, a circulation of the tar in the still would be maintained and no local overheating would take place and thus the "free carbon" content of the pitch would be kept down to a minimum. This would tend to reduce the decomposition or "cracking" of the tar and thus increase the oil yield.

By passing hydrogen through the tar, an intimate mixture of the oils and hydrogen would be obtained. Hydrogenation would then take place in the "Contact Chamber" which would contain the catalytic agent and possibly change the constituents of the distillates to produce a more liquid oil.

ABSTRACT.

Tests were conducted to determine the effect Hydrogen has on Coal Tar and its distillates during the process of distillation.

Heated Hydrogen was passed through the Coal Tar during distillation. The mixed vapors were allowed to come in contact with the catalytic agents at a temperature above the boiling point of the products. The catalytic agents used were aluminum chloride and nickle. Factor studied was the catalytic agent at atmospheric pressure. It would be of interest to have further work done to study the following factors, Coal Tar, temperature of the "Contact Chamber", pressure of the system, Vacuum, atmospheric and above atmospheric, and various other catalytic agents.

From tests conducted would conclude that polymerization has taken place, as is evident by the increase of anthracene salts obtained in the total oil when the catalytic agents were used. Carbon and uncondensable gas are

obtained either as products of decomposition or of polymerization.

PRELIMINARY OUTLINE OF WORK.

OBJECT: To determine the effect hydrogen has upon Coal Tar and its distillates during the process of Distillation; and the percentage of oil yield per gallon of Coal Tar when hydrogenation takes place.

OUTLINE OF PROCEDURE: Heated Hydrogen is to be passed through the Coal Tar during the process of distillation. The mixed vapors are to be allowed to come in contact with a catalytic agent at a temperature above the boiling point of the products.

VARIABLE FACTORS TO BE STUDIED:

1. Coal Tar.
2. Catalytic Agent.
3. Temperature of Entering Hydrogen.
4. Temperature of the "Contact Chamber".
5. Pressure of the System.
   (a) Vacuum.
   (b) Atmospheric.
   (c) Above Atmospheric.

DATA TO BE OBTAINED ON EACH RUN:

% Water in Crude Tar.
% Light Oil Dist. to 205° C.
% Heavy Oil Dist. to 140° F. Pitch.
Final Temp. of Distillation.
M.P. of Pitch. (Water)
% Heavy Oil Dist. to 300° F. Pitch.
Final Temp. of Distillation.

M.P. of Pitch (Air).
Temperature of Hydrogen entering Still.
Specific Gravity of dry Tar @ 60° F.
% of Dry Tar Insoluble in Benzol.
% Ash on dry tar.
Viscosity (Engler) 100_{cc} @ 50° C.
Viscosity (Engler) 100_{cc} @ 115° C.

TEST OF HEAVY OIL (140° F Pitch)

Specified Gravity @ 15.5° C.
% Naphthalene.
Limpid Point.
% Anthracene Salts.
Dry Solids @ 40° F. (4° C)
% Tar Acids.
% Unsulphonated Residue.

Standard Retort Distillation A.S.T.M. D.-7.
% to 170° C.
% to 200° C.
% to 210° C.
% to 235° C.
% to 315° C.
% to 355° C.

Sp. Gr. Fraction (235° C-315° C.) @ 38° C/15.5° C.

TEST OF HEAVY OIL (140° F. Pitch) (to 300° F.A.B.) (Pitch)

Specific Gravity @ 15.5° C.
Limpid Point.
% Naphthalene.
% Anthracene Salts.
Dry Solids @ 40° F (4° C)
% Tar Acids.
% Unsulphonated Residue.

Standard
% to 170° C.
% to 200° C.

Retort Distillation A.S.T.M.

% to 210° C.
% to 235° C.
% to 315° C.
% to 355° C.

Sp. Gr. Fraction (235° C-315° C. @ 38 C/15.5° C.

TEST OF HEAVY OIL (205° to 300° F. A.B. Pitch)

Specific Gravity @ 15.5° C.
Limpid Point.
% Naphthalene.
% Anthracene Salts.
Dry Solids @ 40° F (4° C)
% Tar Acids.
% Unsulphonated Residue.

Standard Retort Distillation A.S.T.M. D-7.

% to 170° C.
% to 200° C.
% to 210° C.
% to 235° C.
% to 315° C.
% to 355° C.

Sp. Gr. Fraction 235° C-315° C. @ 38° C/15.5° C.

% Insoluble in Benzol of 140° F Pitch.
% Insoluble in Benzol of 300° F Pitch.
Melting Point of Bitumen of 300° F Pitch.

% of Total oil yield.
% of 300° F. Pitch.
% to Distillation Loss or Gain.

So far as the writers know, no work has been done on the hydrogenation of Coal Tar and its distillates during the process of distillation. The literature only discusses hydrogenation of aromatic hydrocarbons in a pure state. Ipatiev hydrogenates benzene derivatives by passing them with dry hydrogen over iron, copper or aluminum at a temperature of 400 to 450° C. Sabatier and Senderens showed that at 160° C., benzene is hydrogenized by catalysts, such as finely divided nickel, etc., to cyclo-hexane, and that by passing cyclo-hexane over the same materials at 270 to 280° C., it is reduced to benzene. Smith and Lewcock, have passed benzene through an iron tube heated from 600 to 800° C., and various oxides were used as catalysts, but they soon became coated with carbon. Yields up to 39% diphenyl were obtained. Ubbelohde, St. Philippide, Woronin, Phillips, Bulteel, Day, Hall and Holegreber use hydrogen and a catalytic agent to hydrogenate the Petroleum or its distillates to produce light oils

from the heavier product. The literature discusses to a great extent the hydrogenation of Petroleum, aliphatic hydrocarbon, and only to a very limited extent the hydrogenation of aromatic hydrocarbons.

DESCRIPTION OF RUNS.

RUN 1.

A still (20 c.m. in diameter and 30 cm. high) with a cubical content 9500 c.c. was charges with 7000 grm. of tar. It was heated by means of two ring burners (one at about the level of the tar and the other at the level of the sampling cock which was about 5 or 6 cm. from the bottom) and a rose burner. The still was connected to an air condenser by means of a Hempel distilling tube containing a thermometer. The air condenser delivered into a bottle from which any uncondensed vapors were led into a water condenser.

All joints and possible leaks were plastered up by the following method. A mixture of plaster of paris and asbestos (made up to a putty) was applied to the joints. When this hardened a paste of plaster of paris and glycerine was applied and lastly, if necessary, a coat of water glass.

Run 1 was a regular distillation as is

used to analyze tar (complete tar test). In starting, only the top ring burner was lighted at a low flame and the heat gradually increased. When more heat was required the bottom burner was started and finally, the rose was also used to finish the distillation.

The data and tests obtained are shown in tabulated form. 1,620 c.c. of oil at 60^{o} F, were obtained. The melting point of pitch was 143^{o} F (water) and the vapor temperature was 315^{o} C when the first cut was made. The distillation was carried on and 1530 c.c. of oil at 60^{o} F were obtained, for the second cut. The melting point of pitch was 412^{o} F (AB) and the vapor temperature was 420^{o} C.

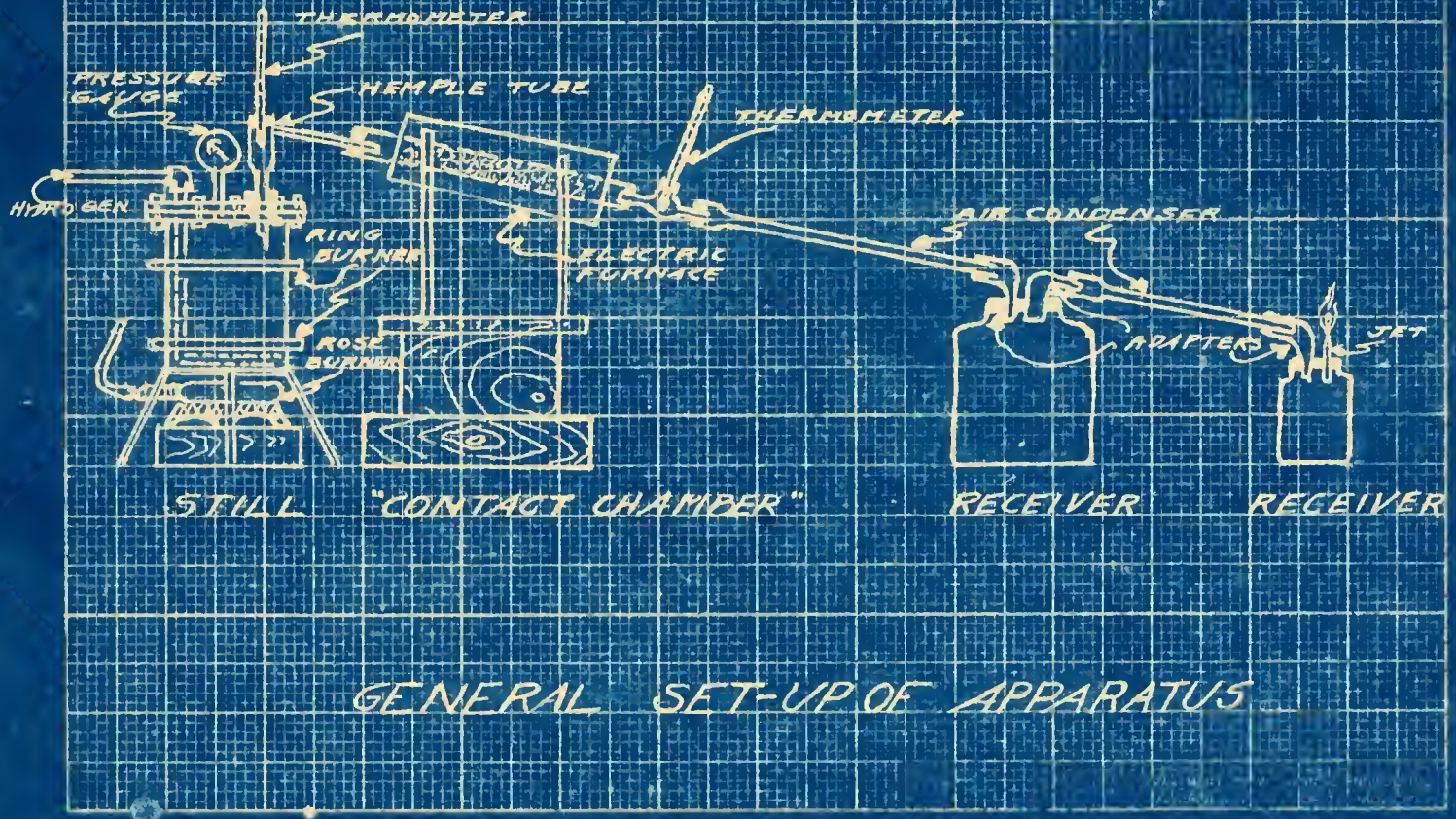
RUN 2.

The apparatus was set up as in Run 1 with the following changes. The receiver at the end of the water cooled condenser was enclosed by a bell glass with open top, with tabulature near bottom and with wide well ground flange. A motor driven vacuum pump was connected to the bell glass by means of the tabulature. It was very dif-

ficult to maintain a vacuum. Leaks were stopped in a similar manner as in Run 1. An attempt was made to carry a high vacuum of about 24" but it was abandoned on account of too much "foaming". A vacuum of 17" was maintained during the process of distillation. Leaks and other trouble made it impossible to complete this distillation. The data obtained was as follows: 1860 c.c. at 60^{o} F. (water) melting point pitch and a vapor temperature of 300^{o} C. Tests are embodied in table.

RUN 3.

Run 3 was the first hydrogenation run. Hydrogen (as obtained in a tank from the Burdette Oxygen Co.,) was washed first with sulphuric acid and then with caustic soda. Regular ground glass stoppered wash bottles were tried but they proved unsuccessful. The slight pressure of the system blew off the stoppers and produced considerable leakage. Ordinary wide mouth bottles with tight rubber stoppers which were wired on proved very successful. The glass tubing that extended into



GENERAL SET-UP OF APPARATUS

A-31

the bottle thru the stopper was forced thru it after the stopper was in place. Of course, care being taken not to break the tubing. This made an air tight stopper.

The hydrogen was led from the washing bottles thru a 1/4" check valve to a 1/4" iron pipe 2 1/2' ft. long which was heated by two wing top Bunsen burners. The pipe was continued into the still being screwed thru the top of it and terminated at the bottom of the still in a perforated ring of 1/4" iron piping. The outside diam. of the ring was about 1" smaller than the inside diam. of the still.

A Hempel distilling tube containing a thermometer led the vapors and hydrogen to the "Contact Chamber". This was a silica tube (1" diam. and 2' long) containing the catalytic material and heated by a standard 110 volt, 5 ampere electric furnace. The catalytic material was made by dissolving 50 grms. of aluminum chloride in water. Asbestos fiber was soaked in this solution for about 12 hrs. and the whole evaporated to dryness. This material was placed in the

silica tube, loosely packed, so as to permit the distillates to pass thru.

This silica tube was joined to a T - tube made of 1/2" glass tubing and with a bulb at the junction of the legs. The bulb gave ample room for a thermometer bulb to be placed in it without forming too great an obstruction to the stream of distillate. The temperature of the exit vapors and gas was kept about 60° C above the temperature of vapors and gas leaving the still.

This T tube was followed by two air condensers. The water condenser used in previous runs had to be discarded because it was being continually plugged with solid distillate and no flame could be applied to it to melt same. As before, a bottle receiver connected the two condensers. The end receiver i. e. the receiver at the end of the 2nd air condenser, was supplied with a glass jet for burning the excess hydrogen and uncondensable gas. The gases coming off were not analyzed, but due to the luminosity of the flame one would be led to assert that a gas other than pure hydro -

gen was being burned; probably hydrocarbons mixed with hydrogen.

Data obtained: 1842 c.c. at 60° F to 147° F (water) melting point pitch was distilled. Final temperature of distillation was 310° C. Tests in table.

Due to an accident, the distillation had to be discontinued. The catalytic material used in the contact chamber swelled considerably, and had a metalic luster, shown that aluminum chloride had been reduced to the metal aluminum. Carbon was deposited on it to such an extent that no distillate could possibly pass thru. A hydrogen flame was burning to the end. It was not anticipated by the workers that it was possible for hydrogen to pass thru the plug while the distillate was held back. As a result of the pressure which was built up in the still by the accumalated vapors of distillation((the check valve on the entrance pipe prevented the back pressure to force the contents of the still back into the wash bottles), the contents of the still was blown out thru the Hempel tube and ignited, that

being the weakest point and the line of least resistence. It was therefore decided in subsequent runs to connect a pressure gauge to the still to indicate an increased pressure if it occurred and pumice stone was substituted for asbestos fiber.

RUN 4.

Except for the catalytic material and the pressure gauge Run 4 was identical to Run 3. About 100 grms. of nickel nitrate was dissolved in water and pieces of pumice stone were left to soak in it for 20 hrs. After this, the whole was evaporated to dryness. The pieces of pumice were then ignited giving nickelic oxide in a finely divided state in the pumice. The tube of the furance was then packed loosely with this material and the distillation carried on as in the previous run.

Data obtained: 1671 c.c. at 60^{o} F. to 130^{o} F (water) melting point pitch were distilled with final temperature of 395^{o} C. Second cut was 1716 c.c. at 60^{o} F to 305^{o} F (air) melting point pitch with final temperature of distillation of

428° C.

RUN 5.

This run was made with 100 grms. of anhydrous aluminum chloride in still and aluminum chloride (prepared with pumice) in the "Contact Chamber". Other conditions were identical to previous runs.

Data obtained : Light Oil to 162° F (water) pitch at 60° F - 1615 c.c. Final temperature of cut 370° C. Heavy Oil from 162° F (water) pitch to 391° F (air) pitch at 60° F 1379 c.c. Final temperature of distillation 391° C. Other tests in table.

RUN 6.

To ascertain whether the aluminum chloride in the still or in the "Contact Chamber" produced a change in the distillates, it was deemed necessary to make a run with aluminum chloride in the still, and no catalytic material in the "Contact Chamber". This was the only difference between Run 6 and previous runs.

Data obtained :- Light Oil to 153° F (water) pitch at 60° F 1408 c.c. Final temperature of cut 314° C. Heavy Oil from 153° F (water) pitch to 342° F (air) pitch at 60° F 1553 c.c. Final temperature of distillation 425° C. Other tests in table.

RUN 7.

As a means of checking up, Run 7 was made without passing hydrogen thru the system and no catalytic material in the "Contact Chamber" or in the still; other conditions were the same as in the other runs.

Data obtained: Light Oil to 137° F (water) pitch at 60° F - 1575 c.c. Final temperature of cut 365° C. Heavy oil from 137° F (water) pitch to 378° F (air) 1704 c.c. at 60° F. Final temperature of distillation 445° c.c. Other tests in table.

TEST OF TAR RUN NO.	1	2	3	4	5	6	7
% Water	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C.C.Light Oil Dist. to 140°F. Pitch at 60°F.	1620	1860	1842	1671	1615	1408	1575
% Light Oil Dist. to 140°F. Pitch-Fract. A (by vol.)	27.7	31.8	31.7	28.5	27.6	24.1	26.9
Final Temp.of Distillation	315°C.	300	310	395	370	314	365
M.P.of Pitch (Water)	143	153	147	139	162	153	137
C.C.Hy.Oil Dist.from 140°F. Pitch to 300°F.Pitch at 60°F-	1530	-	-	1716	1379	1553	1704
% Heavy Oil Dist. from 140°F.Pitch to 300°F.Pitch (Fract.B) by volume	26.1	-	-	29.3	23.7	26.6	29.2
C.C.Heavy Oil Dist. to 300°F.Pitch by volume at 60°F.	3150	-	-	3387	2994	2961	3279
% Heavy Oil Dist.to 300°F. Pitch (Fract.C) by volume	53.8	-	-	57.8	51.3	50.7	56.1

TEST OF TAR RUN NO.	1	2	3	4	5	6	7
Final Temp.of Distillation	420°C.	-	-	428	445	425	445
M.P. of Pitch(Air)- °F.	412	-	-	405	391	342	378
TEST OF DRY TAR							
Spec.Grav. at 60°F.	1.196	1.196	1.196	1.196	1.196	1.196	1.196
% Insoluble in Benzol	10.37	10.37	10.37	10.37	10.37	10.37	10.37
% Ash	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Viscosity(Engler)100cc.@50°C	314	314	314	314	314	314	314
" " " 115 "	32	32	32	32	32	32	32
TEST OF FRACTION A - LIGHT OIL DIST.TO 140°F.PITCH							
Specific Gravity @ 15.5°C.	1.043	1.054	1.063	1.056	1.077	1.067	1.061
Limpid Point	108	101	103	103	101	106	105
% of Solid up to 200°C.	0.4	0.6	0.5	0.9	0.4	2.5	0.8

TEST OF FRACTION A (Cont'd)

	1	2	3	4	5	6	7
% of Naphthalene (Fract. 200-250°C.)	26.3	22.0	22.0	24.0	19.0	24.2	23.4
% of Solids (Fract.250-300°C.)	1.3	0.8	1.9	0.8	1.4	0.2	0.3
% of Anthracene Salts (Fract.300-390°C.)	3.3	5.4	6.5	5.3	6.6	4.3	5.0
Dry Solids	21.2	16.3	20.8	20.8	20.0	21.3	22.6
% Tar Acids	6.8	6.8	6.0	6.0	5.0	6.5	6.8
% Unsulphonated Residue	1.0	1.0	0.2	0.2	0.2	0.2	0.2
STANDARD (% to 170°C.)	0.3	0.2	0.0	0.4	0.0	0.0	0.0
RETORT (% " 200 ")	3.0	1.2	1.0	1.4	1.1	2.5	0.8
DISTILLATION (% " 210 ")	5.0	2.7	2.6	3.3	3.8	5.0	2.5
A.S.T.M. (% " 235 ")	47.7	45.5	36.8	37.8	30.8	42.8	37.4
D-7 (% " 315 ")	88.3	84.3	79.2	80.5	72.0	76.2	62.8
(% " 355 ")	97.0	94.5	94.0	94.0	88.3	90.6	85.8

TEST OF FRACTION A (Cont'd)

		1	2	3	4	5	6	7
Spec.Grav.Fraction 235-315°C at 38°C/15.5°C.		1.036	1.035	1.039	1.037	1.038	1.036	1.035
BULB DISTILLATION	(% to 170°C.)	1.5	0.0	0.0	0.0	3.0	3.0	0.0
	(% " 200 ")	3.5	2.1	3.5	3.0	6.0	10.0	2.0
	(% " 210 ")	9.0	8.1	10.0	9.0	10.0	19.0	8.0
	(% " 235 ")	49.0	46.8	42.0	47.0	37.0	52.0	39.0
	(% " 250 ")	66.0	62.3	54.0	61.5	52.5	65.0	59.5
	(% " 300 ")	84.0	78.5	75.0	78.0	66.5	80.0	73.0
	(% " 315 ")	89.5	86.4	81.0	81.0	73.0	85.0	75.0
	(% " 355 ")	(95.0) (340°C)	(96.7) (340°C)	91.0	91.5	86.0	92.0	83.0
	(% " 390 ")	-	-	(95.0 (370°C)	(96.0 (380°C)	90.0	94.0	90.0

TEST OF FRACTION B - HEAVY OIL
DIST.FROM 140°F.Pitch 300°F.A.B.PITCH

Specific Gravity @15.5°C.	1.145	-	-	1.142	1.142	1.145	1.148
Limpid Point °F.	136	-	-	126	142	140	137

TEST OF FRACTION B (Cont'd)

	1	2	3	4	5	6	7
% Solids in fraction up to 200°C.	0.0	-	-	0.0	0.0	0.0	0.0
% of Naphthalene Fract. 200-250°C.	0.0	-	-	0.0	0.0	0.2	0.3
% of Solids fraction (250-300°C.)	0.3	-	-	0.2	0.2	0.2	0.3
% of Anthracene Salts (300-390°C.)	9.5	-	-	9.2	10.0	7.5	6.3
Dry Solids	9.5	-	-	9.4	11.0	6.8	5.3
% Tar Acids	2.2	-	-	2.8	2.0	2.0	4.0
% Unsulphonated Residue	0.2	-	-	0.0	0.0	0.0	0.0
(% to 170°C.)	0.0	-	-	0.0	0.0	0.0	0.0
STANDARD (% " 200 ")	0.0	-	-	0.0	0.0	0.5	0.0
RETORT (% " 210 ")	0.0	-	-	0.2	0.0	1.0	0.0
DISTILLATION (% " 235 ")	0.0	-	-	0.9	0.0	2.0	0.8
A.S.T.M. (% " 315 ")	3.0	-	-	9.8	7.0	20.0	8.0
D-7 (% " 355 ")	49.6	-	-	41.8	36.2	51.8	33.2
(% " 390 ")	75.0	-	-	68.0	71.4	73.5	60.0

		1	2	3	4	5	6	7
Spec. Grav. Fract. 235-315°C. at 38°C/15.5°C.		Not sufficient			Not sufficient			
BULB DISTILLATION	(% to 170°C.)	0.0	-	-	0.0	0.0	2.0	0.0
	(% " 200 ")	0.0	-	-	1st Drop	0.0	2.5	0.0
	(% " 210 ")	0.0	-	-	1.0	0.0	3.5	0.0
	(% " 235 ")	0.0	-	-	2.0	1.5	6.0	3.0
	(% " 250 ")	1.0	-	-	3.0	2.5	8.0	5.0
	(% " 300 ")	7.0	-	-	8.0	9.0	20.0	14.0
	(% " 315 ")	12.5	-	-	14.0	15.0	25.5	20.0
	(% " 355 ")	44.5	-	-	40.0	41.0	52.5	38.0
	(% " 390 ")	73.0	-	-	68.0	71.0	74.0	58.0
					435°F-95.0			

TEST OF FRACTION C
HEAVY OIL DIST. TO 300°F. (A.B.PITCH)

Specific Gravity @15.5°C.	1.090	-	-	1.099	1.109	1.107	1.107
Limpid Point	108	-	-	136	135	137	133
% Solids in fraction up to 200°C.	0.4	-	0	0.4	0.2	0.3	0.2
% Naphthalene (fraction 200-250°C.)	10.5	-	-	10.5	6.4	10.3	8.5

TEST OF FRACTION C (Cont'd)

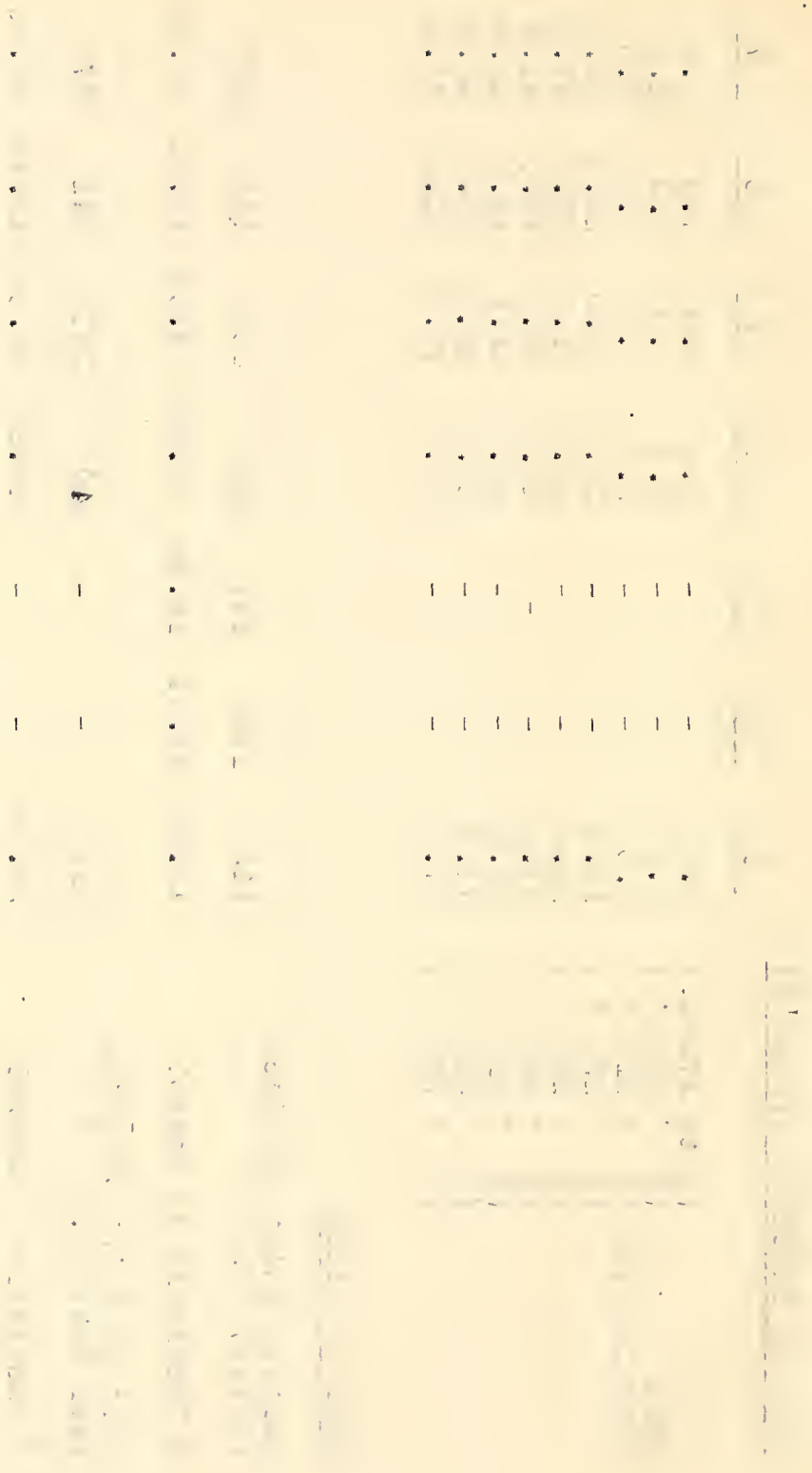
	1	2	3	4	5	6	7
% Solids (fraction 250-300°C.)	0.5	-	-	0.2	3.2	2.3	2.8
% of Anthracene Salts (300-390°C.)	6.6	-	-	7.5	8.3	6.3	5.0
Dry Solids	8.0	-	-	7.0	3.5	5.8	3.8
% Tar Acids	3.2	-	-	4.5	3.6	4.0	5.5
% Unsulphonated Residue	0.6	-	-	0.1	0.1	0.1	0.1
STANDARD RETORT DISTILLATION A.S.T.M. D-7 (% to 170°C.)	0.0	-	-	0.0	0.0	0.0	0.0
(% " 200 ")	0.0	-	-	0.7	0.4	1.0	0.2
(% " 210 ")	1.3	-	-	2.1	0.8	2.4	1.1
(% " 235 ")	9.4	-	-	12.6	6.7	15.0	8.6
(% " 315 ")	47.7	-	-	45.6	40.0	48.0	39.9
(% " 355 ")	68.9	-	-	71.2	61.2	71.4	62.4
(% " 390 ")	84.1	-	-	-	81.7	-	73.8
Spec. Grav. Fraction 235-315°C at 38°C/15.5°C.	1.037	-	-	1.032	1.038	1.037	1.038

TEST OF FRADTION C(Cont'd)

		1	2	3	4	5	6	7
BULB DISTILLATION	(% to 170°C.)	0.0	-	-	0.0	0.0	1.0	0.0
	(% " 200 ")	4.0	-	-	3.0	1.0	5.0	2.0
	(% " 210 ")	5.0	-	-	5.0	4.5	9.0	5.0
	(% " 235 ")	18.0	-	-	19.0	12.0	20.5	18.0
	(% " 250 ")	28.5	-	-	28.0	21.0	30.0	27.0
	(% " 300 ")	47.0	-	-	42.5	40.0	45.0	42.0
	(% " 315 ")	51.5	-	-	46.5	45.5	49.5	46.0
	(% " 355 ")	72.0	-	-	65.0	63.0	68.0	63.0
	(% " 390 ")	87.0	-	-	78.0	79.0	81.0	77.0

TEST OF PITCH

Melting Point of Pitch (Water) °F.	143	153	147	139	162	153	137
% Insoluble in Benzol	17.38	16.01	18.34	18.83	19.63	18.21	16.98
Melting Point of Pitch (Air Bath °F.)	412	-	-	405	391	342	378
% Insoluble in Benzol	56.34	-	-	49.99	53.63	45.48	48.36



DISTILLATION CURVES.

These curves were drawn using temperatures on the y-axis and total percentage distillation on the x-axis.

Comparing curves of fraction A of Run 1 and 2, the boiling range of the fraction has been slightly increased above 250° C, which would indicate that a larger portion of oil was obtained in Run 2, between 250 and 390 than in Run 1. From this we would expect a slight increase of anthracene salts in fraction 300-390° C which is shown to be the case when comparing the anthracene yield in the table. This was due to the vacuum which effected the vapor pressure of the tar.

Comparing curves of fraction A of Run 1 and 3, we find that the difference of the curves is more marked than in the previous case. The boiling range has been increased between the temperatures of 310 and 390, showing that oils of higher boiling range must have been obtained in this run. We would expect an increase in anthracene salts in Run 3 over Run 2. Anthracene salts yield shown in table bear out this conclusion.

In comparing Run 1 and 4, fraction A, we note that the difference pointed out in the above case is not as great as Run 3.

Continuing the comparison, Run 5 shows a greater difference than in Run 3.

Curve of Run 6, shows the smallest difference so far noted, although the lower end shows a greater quantity of lower boiling oils.

Curve of Run 7, shows a difference almost equal to that of Run 4.

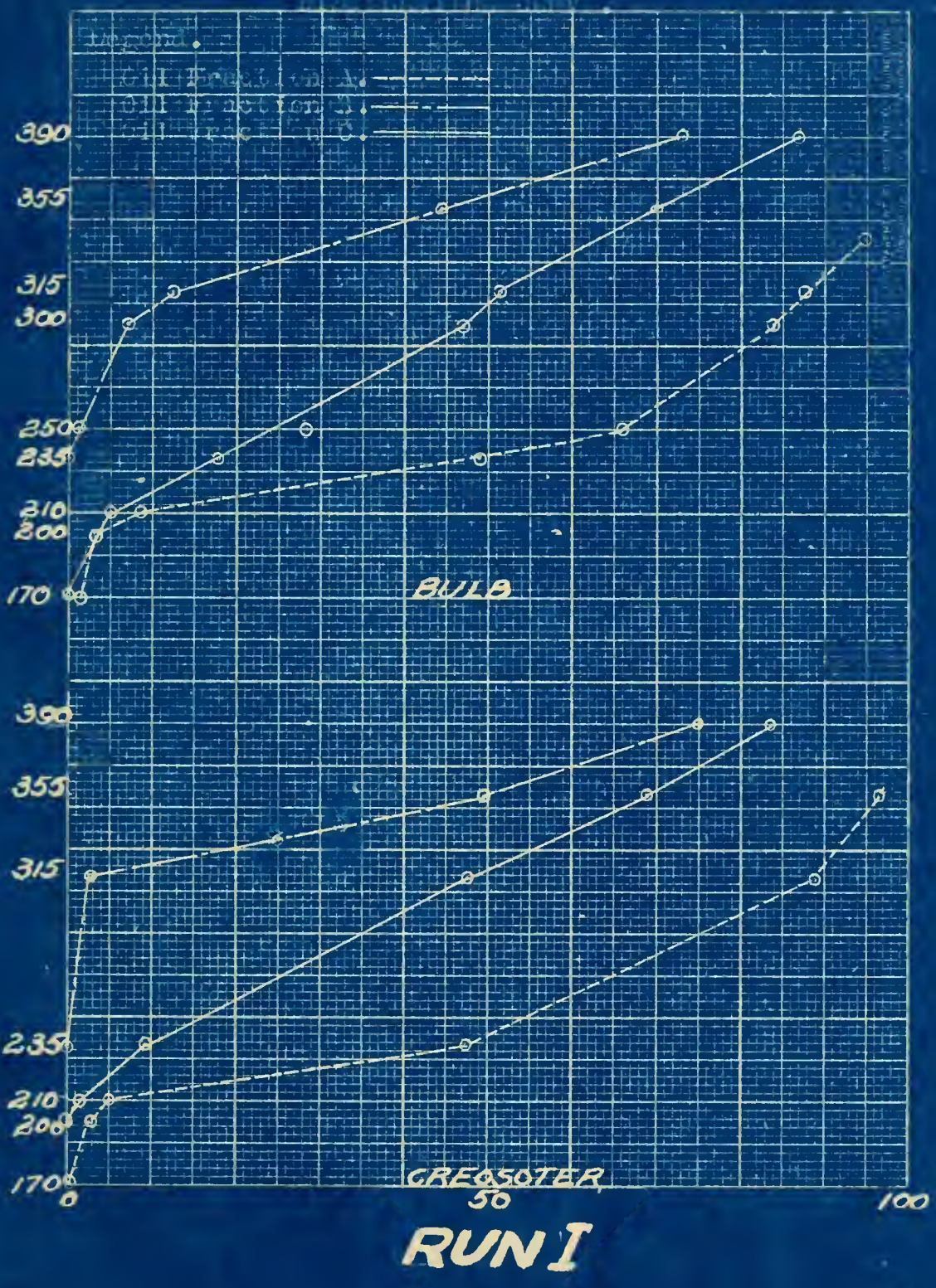
Comparing curves of Run 1 and 4, fraction B, we note that they are approximately the same.

Curve B, of Run 5, indicates to be a higher boiling range oil and one would expect to find more anthracene salts. Table shows increase of anthracene salt yield over Run 1.

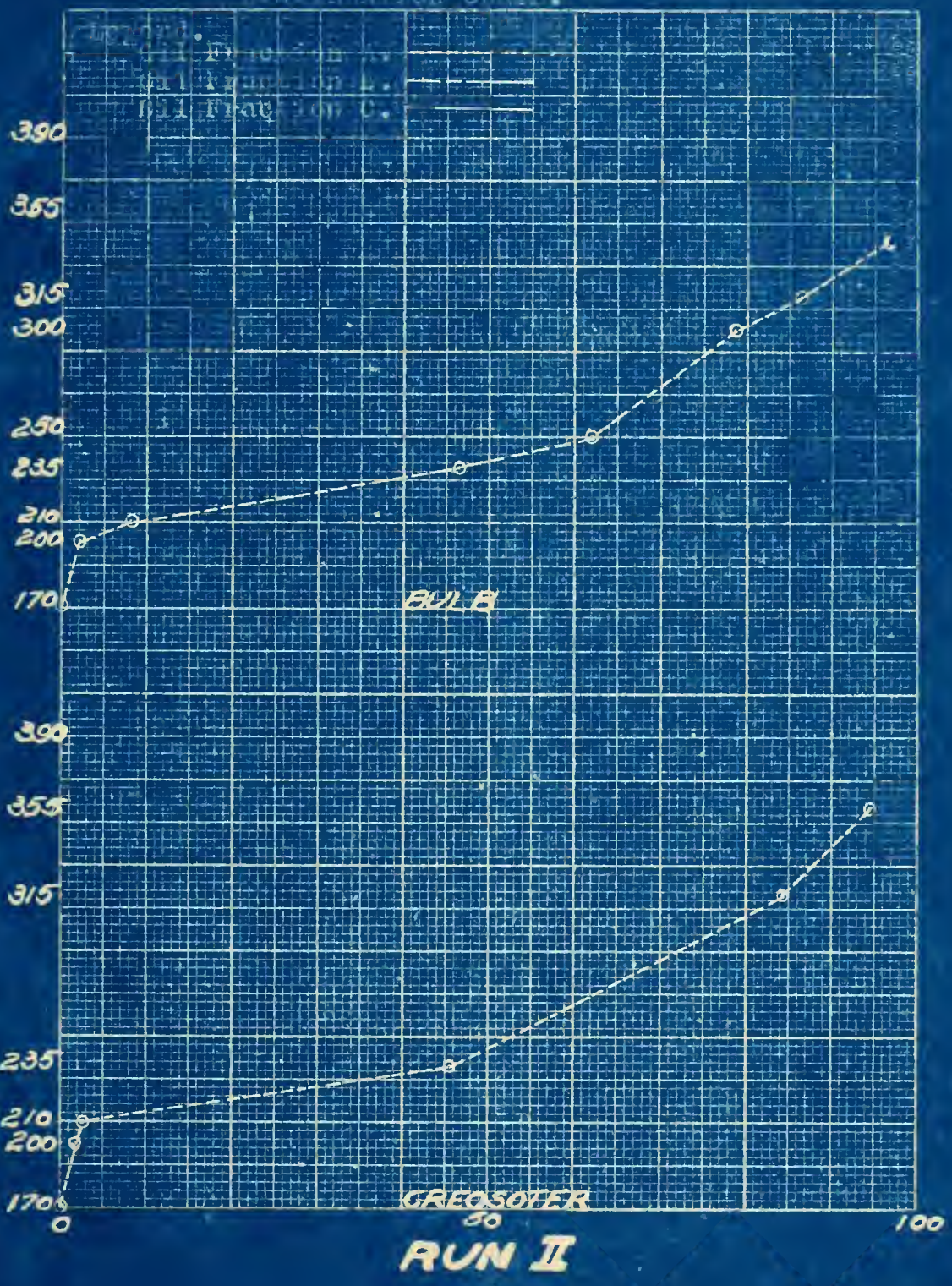
Curve B of Run 6 points out that the oil is of a lower boiling range. Smaller yield of anthracene salts would be expected in this oil. Results showed in table bear out this view.

Curve B of Run 7, shows that the boiling range is considerably lower than in Run 1 up to

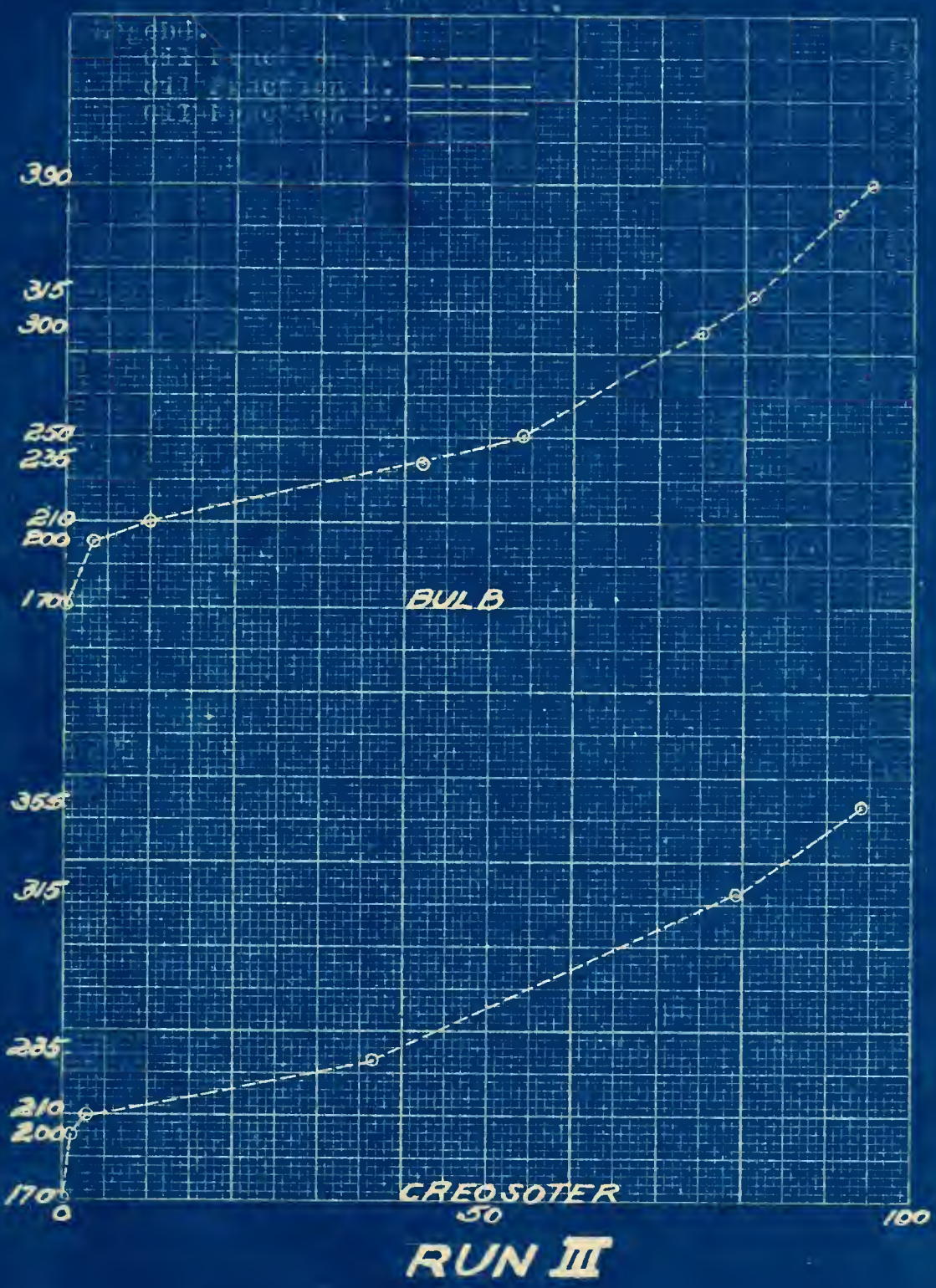
315° C and then becomes an oil of a higher boiling range. This indicates á mixture of lower and higher boiling oils. One would expect from such an oil a low yield of anthracene salts. Anthracene content of this fraction of these runs, (shown in table) bears this out.


390
355
315
300
250
235
210
200
170
BULB
390
355
315
235
210
200
170
0
CREOSOTER
50
100

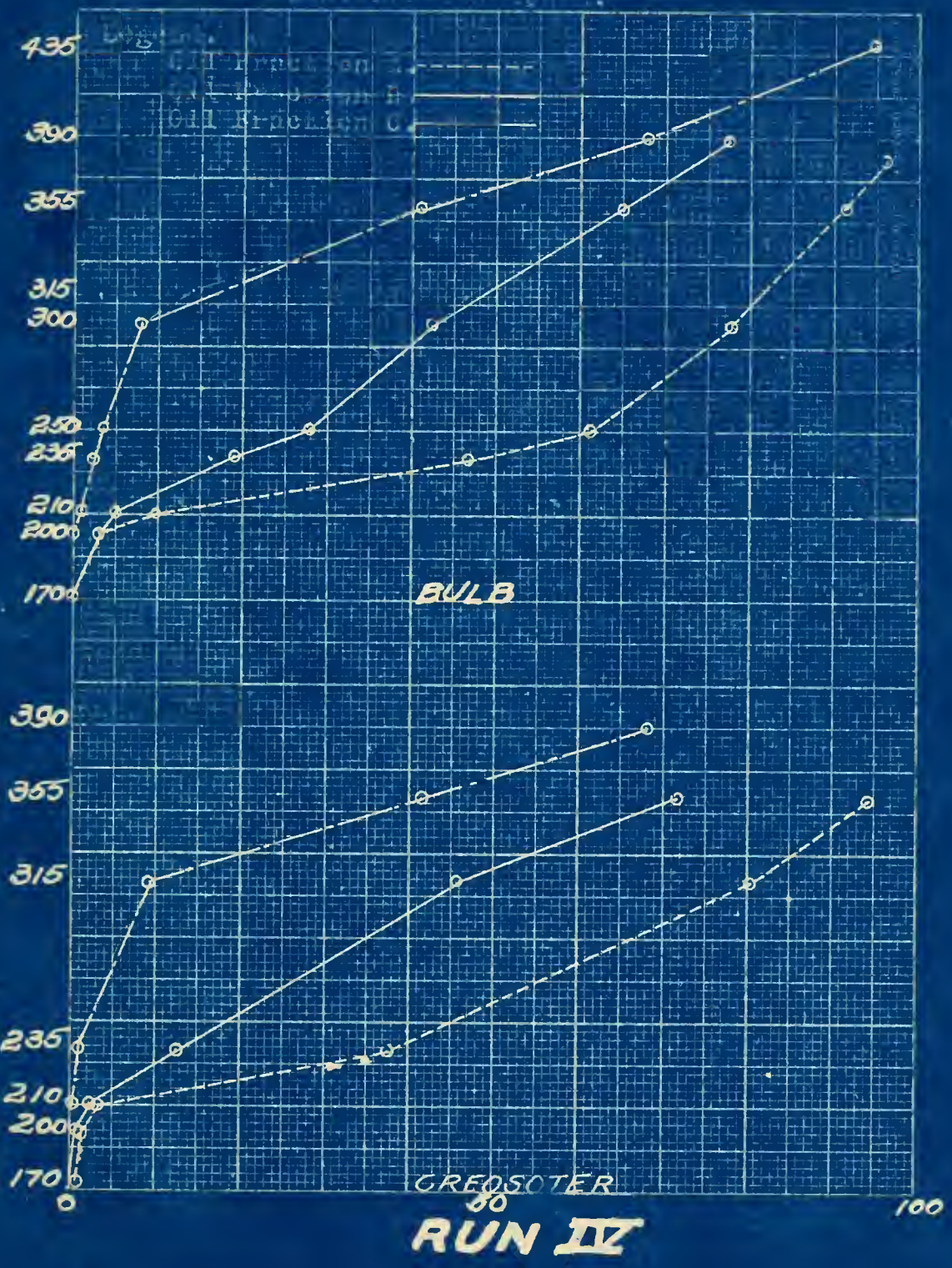
RUN I

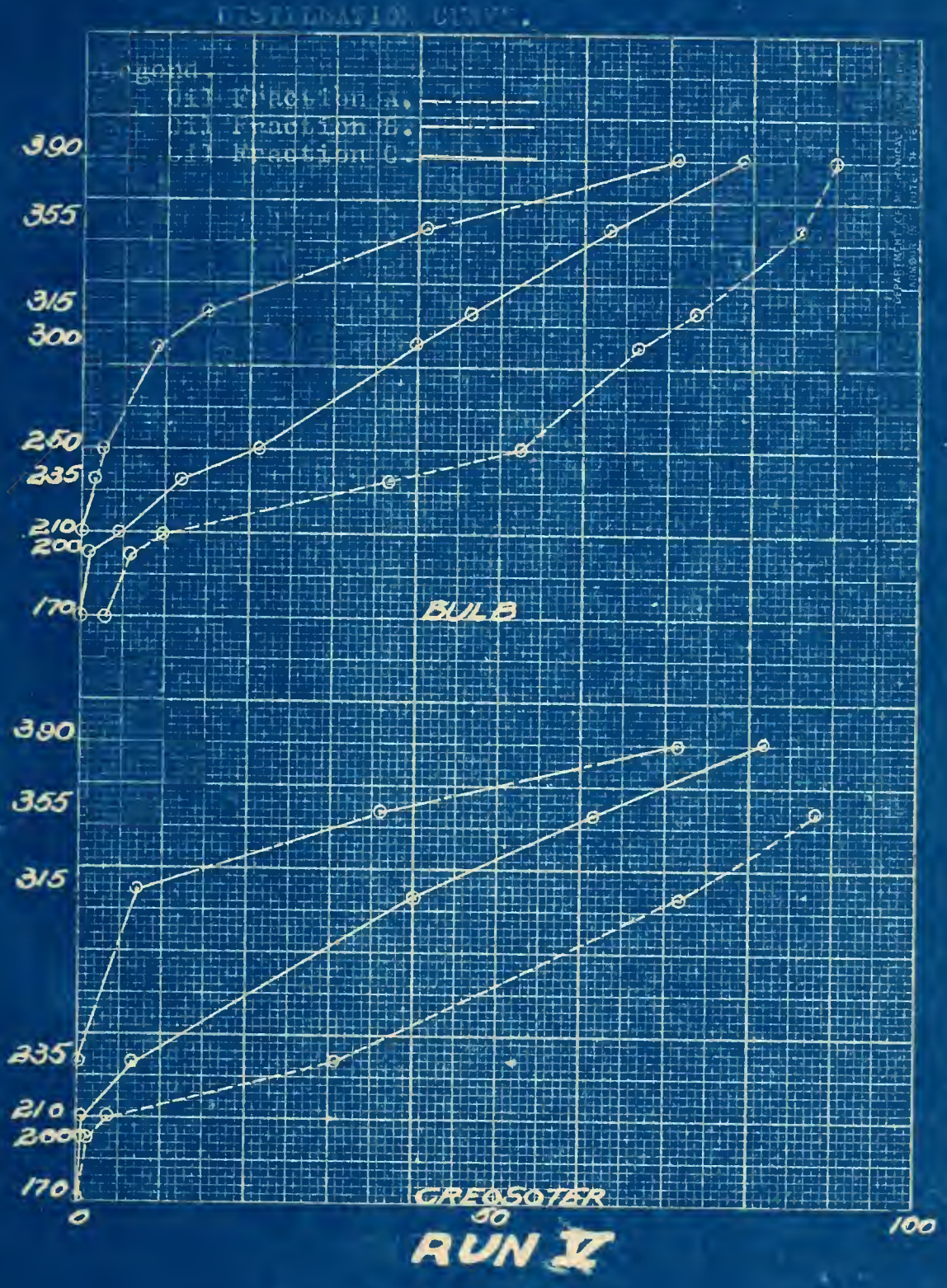

390
355
315
300
250
235
210
200
170
BULB
390
355
315
235
210
200
170
CREOSOTER
0
50
100

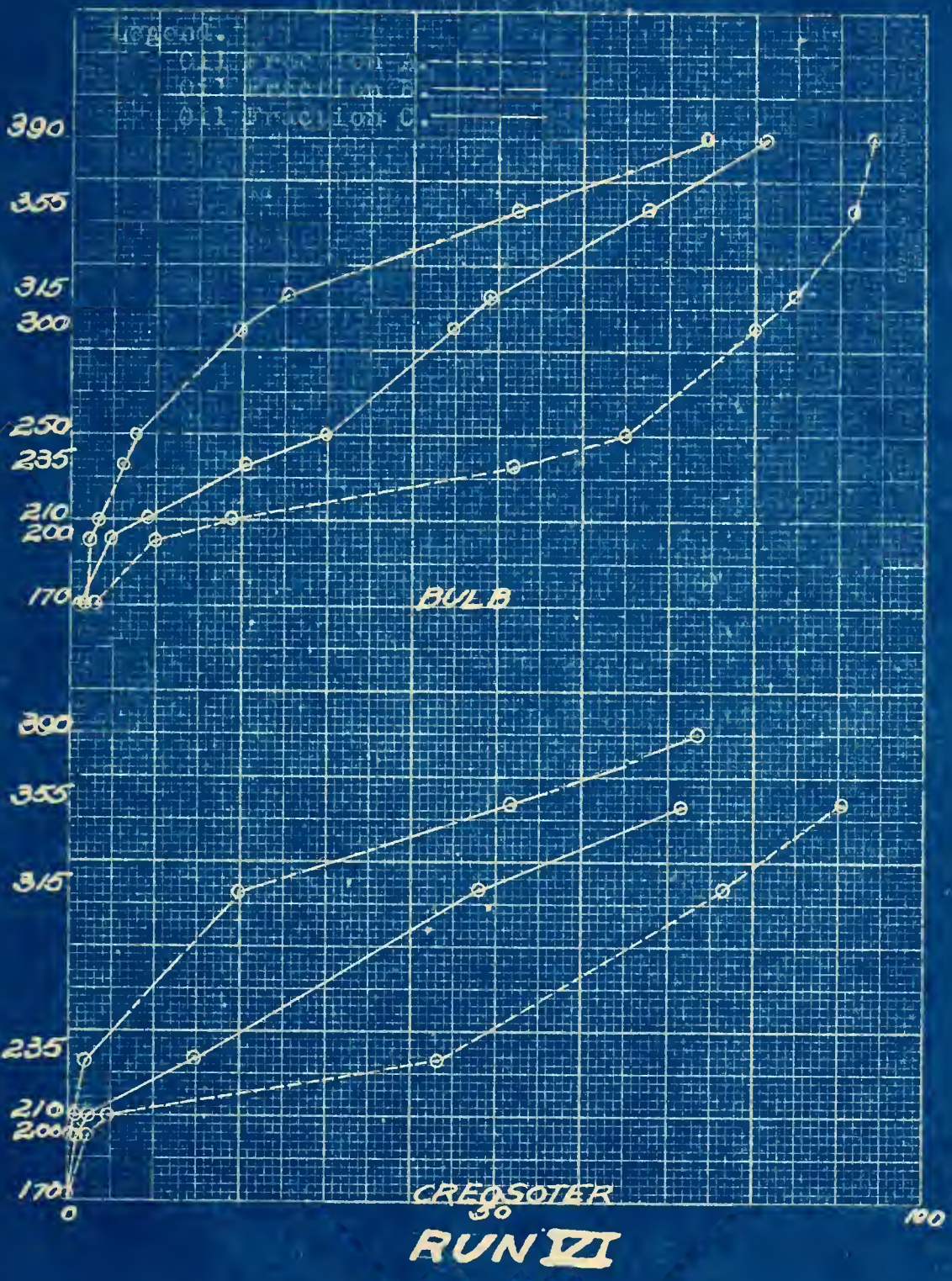
RUN II

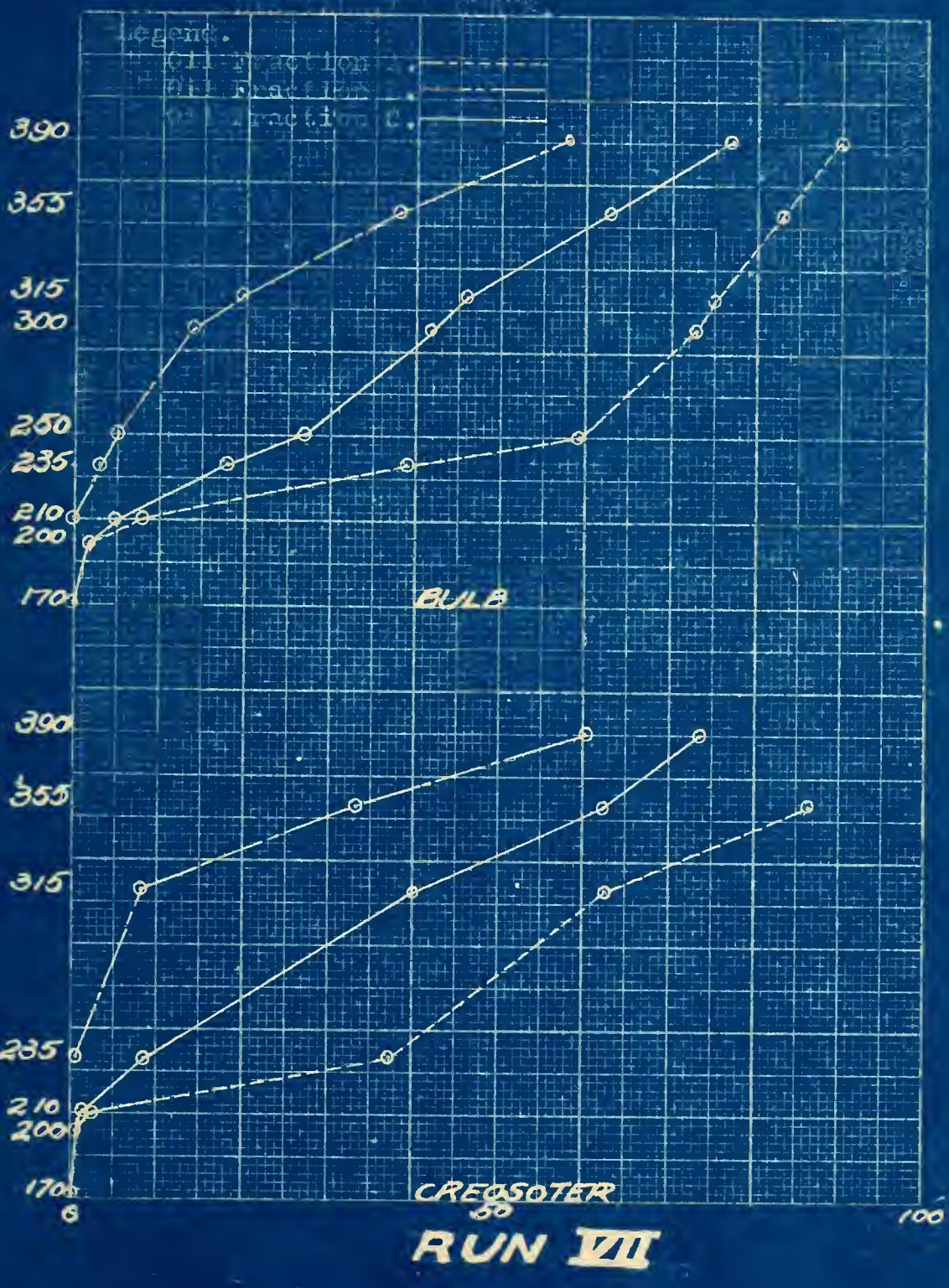

390
315
300
250
235
210
200
170
BULB
365
315
235
210
200
170
0
CREOSOTER
50
100

RUN III


435
390
365
315
300
250
235
210
200
170
BULB
390
365
315
235
210
200
170
0
50
100
CREOSOTER
RUN IV


DISTILLATION CURVE.
Legend
Oil Fraction A.
Oil Fraction B.
Oil Fraction C.
390
355
315
300
250
235
210
200
170
BULB
390
355
315
235
210
200
170
CREOSOTER
0
50
100
RUN V


Legend.
Oil Fraction A.
Oil Fraction B.
Oil Fraction C.
390
355
315
300
250
235
210
200
170
BULB
300
355
315
235
210
200
170
0
50
100
CREOSOTE
RUN VI


390
355
315
300
250
235
210
200
170
BULB
390
355
315
235
210
200
170
CREOSOTER
0
50
100

RUN VII

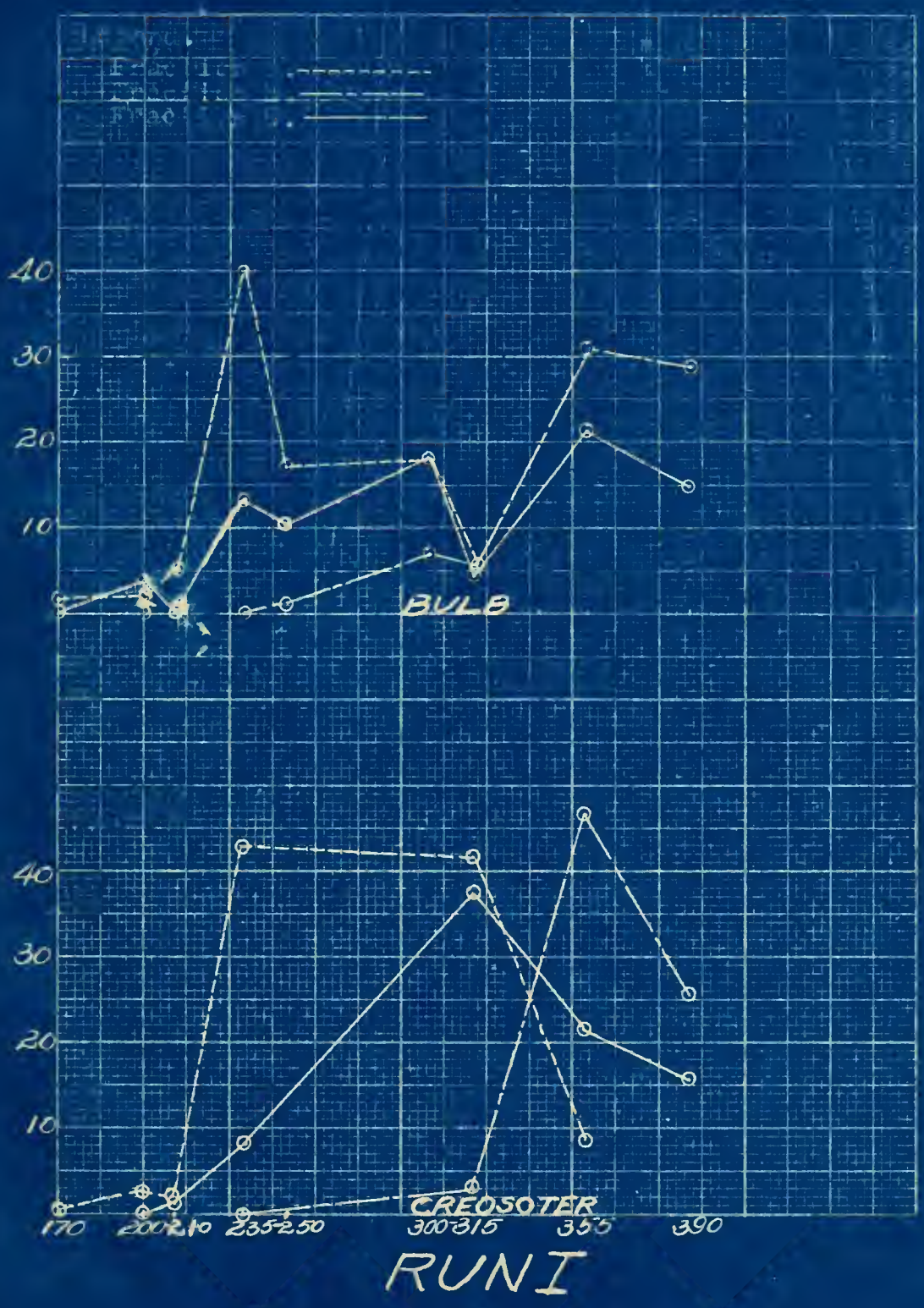
PER CENT OF OIL PER TEMPERATURE DIFFERENTIAL.

These curves were made using the x-axis for temperatures and the y-axis as the difference between per centage of distillate for each temperature differential.

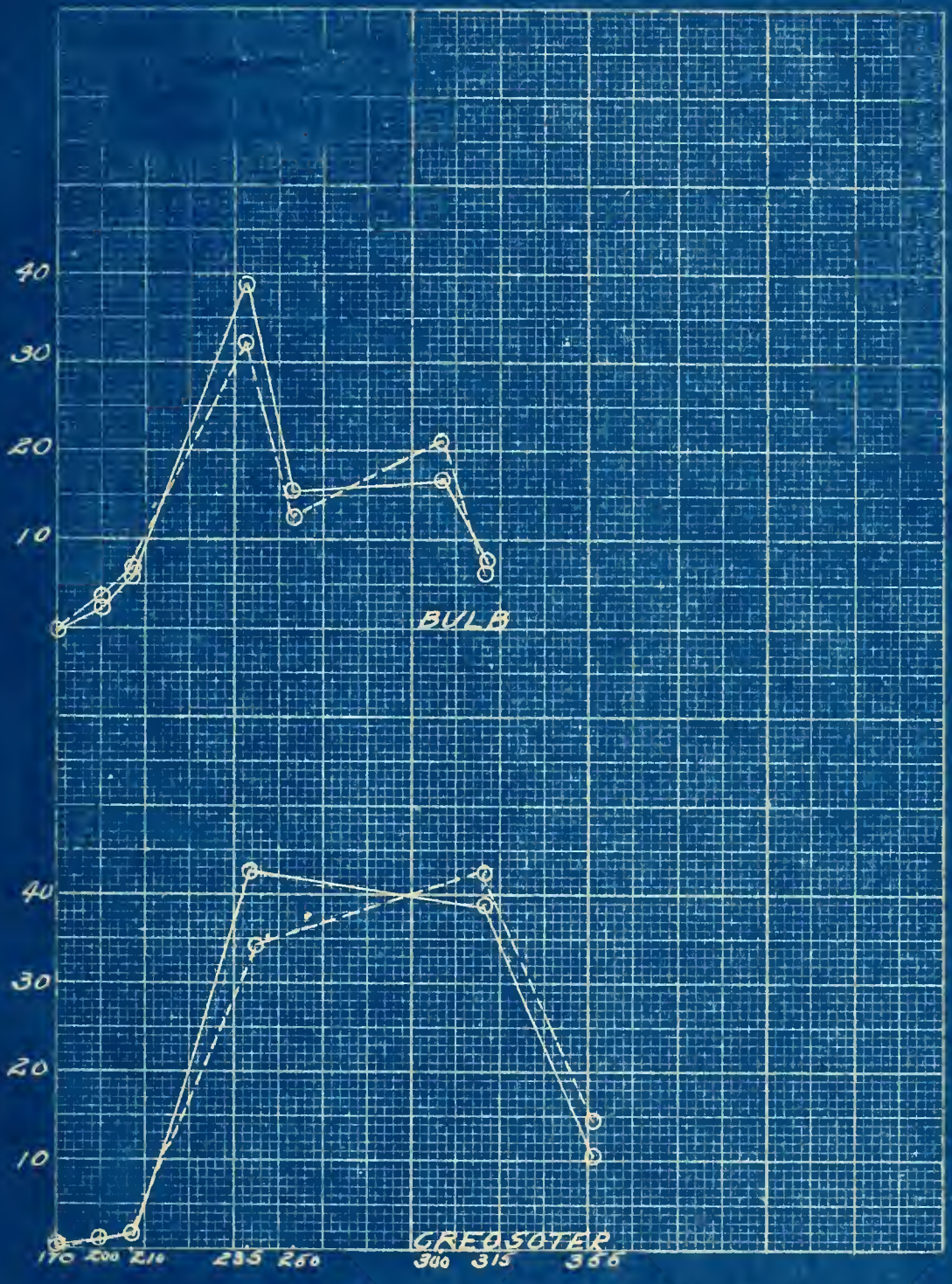
They show the same differences as the distillation curves.

In comparing the per cent of oil per temperature differential curves of Fraction A, it is to be noted that the portion of curves up to 250° C indicate that the naphthalene content of the oils obtained gradually decrease from Run No.1 to inclusive Run 5. The curve of Run 5 indicates the lowest naphthalene content for the oils of Fraction A. The naphthalene content of Run 6 is increased above that of Run 5 but it is lower than that of Run 4 and Run 7. The curve of Run 7 indicates that the naphthalene content is increased over that of Run 6. Multiplying the No. of c.c. of the fraction A with the per cent of naphthalene salts obtained we obtain for Run No.1 ·426 grms; for Run 2, 407 grms; for Run 3, 405

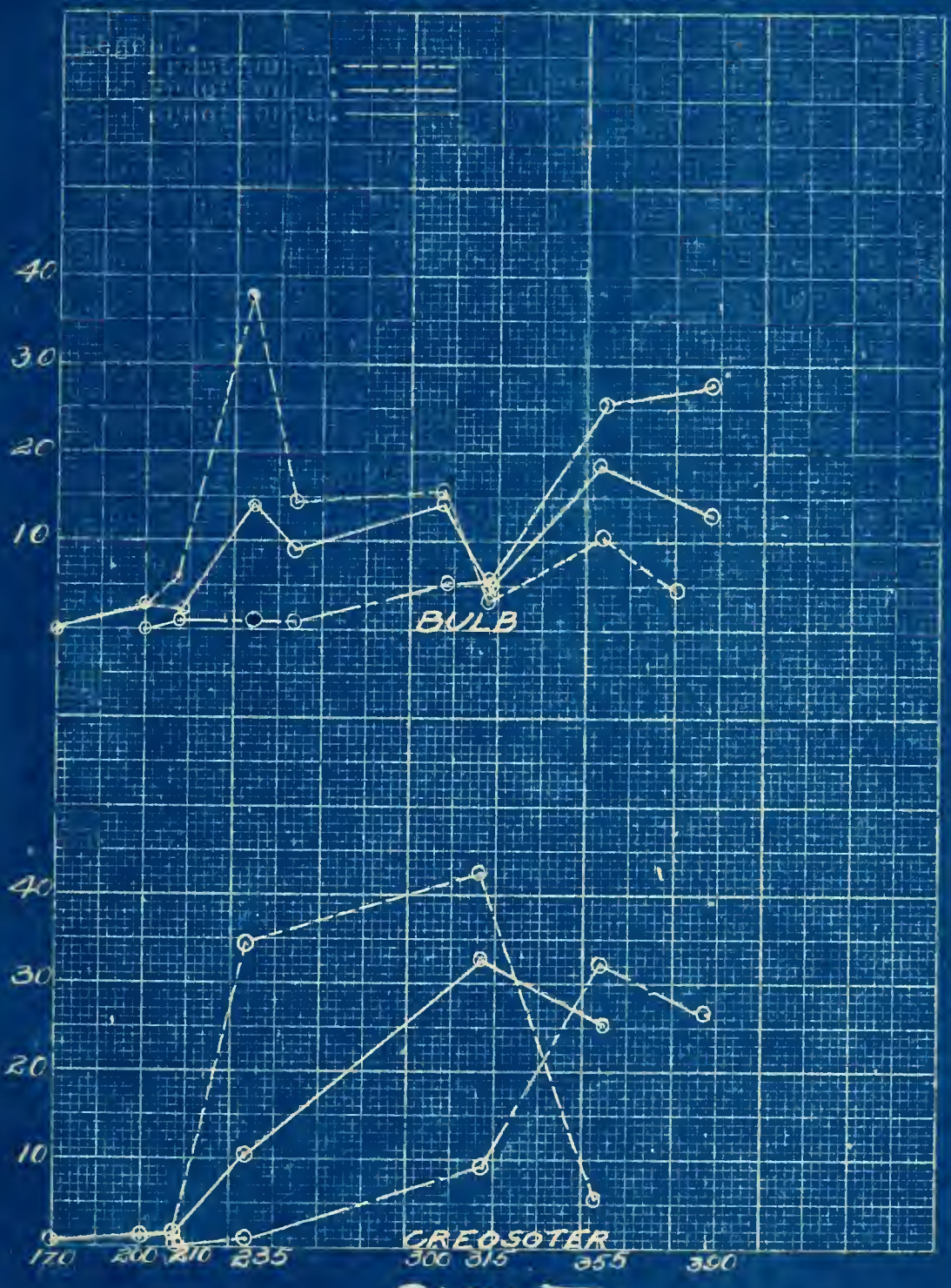
grms; for Run 4, 401 grms; for Run 5, 307 grms; for Run 6, 339 grms; and for Run 7, 368 grms. The distillation curves and the % of naphthalene salts obtained indicate that the naphthalene fraction was not affected by the hydrogen when the catalytic agent was used in the contact chamber. That the naphthalene fraction was affected when the catalytic agent aluminum chloride was used in the tar.


40
30
20
10
BULB
40
30
20
10
CREOSOTER
170
200-210
235-250
300-315
355
390

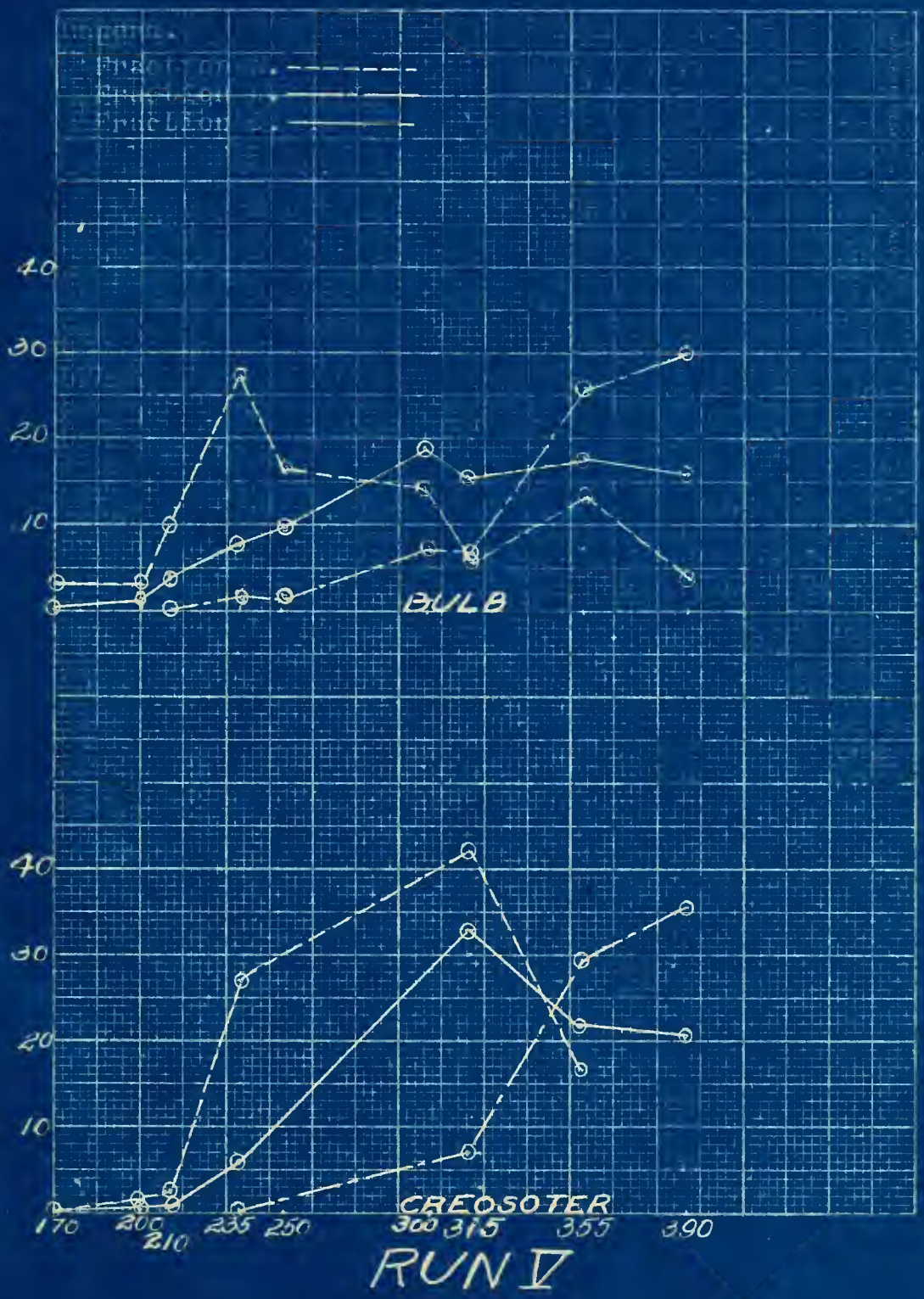
RUN I



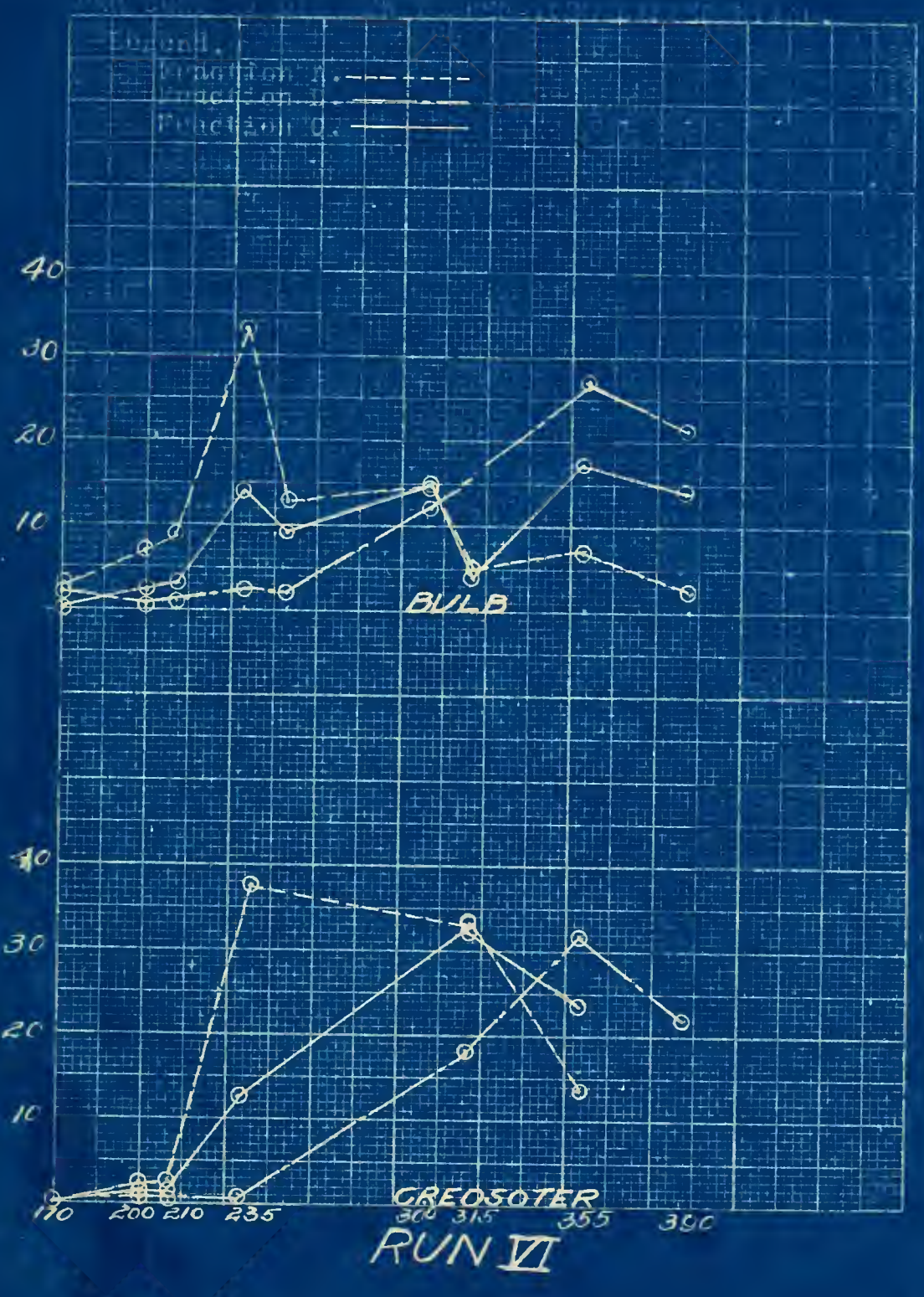
RUN II —
RUN III ---- FRACTION A.


40
30
20
10
BULB
40
30
20
10
CREOSOTER
170
200
210
235
300
315
355
390

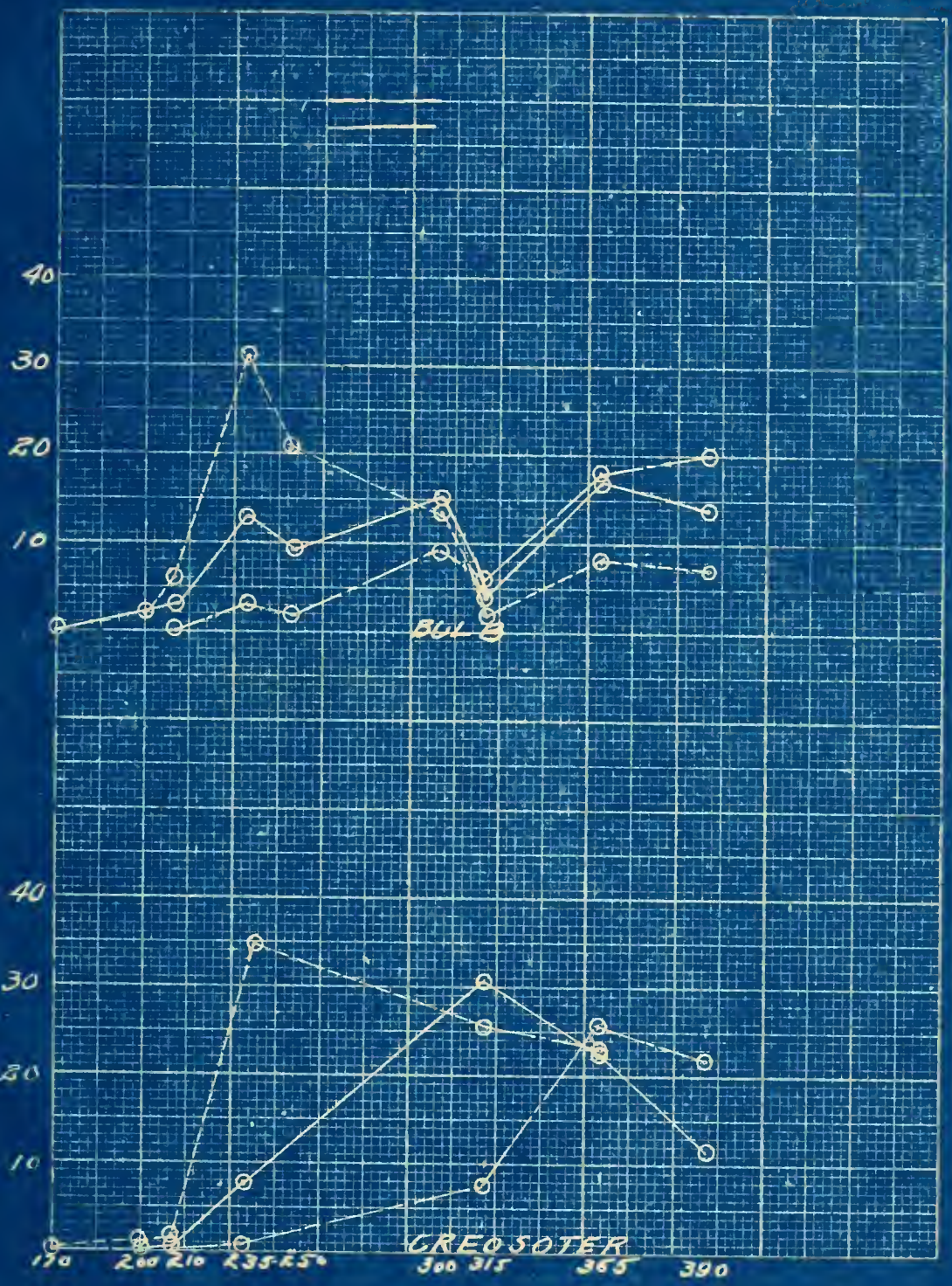
RUN IV


40
30
20
10
BULB
40
30
20
10
CREOSOTER
170
200
210
235
250
300
315
355
390

RUN V


Benzol.
Fraction B.
Fraction C.
Fraction D.
40
30
20
10
BULB
40
30
20
10
170
200
210
235
300
315
355
390
CREOSOTER

RUN VI


40
30
20
10
BULB
40
30
20
10
CREOSOTER
170
200
210
235-245
300
315
365
390

RUN VII

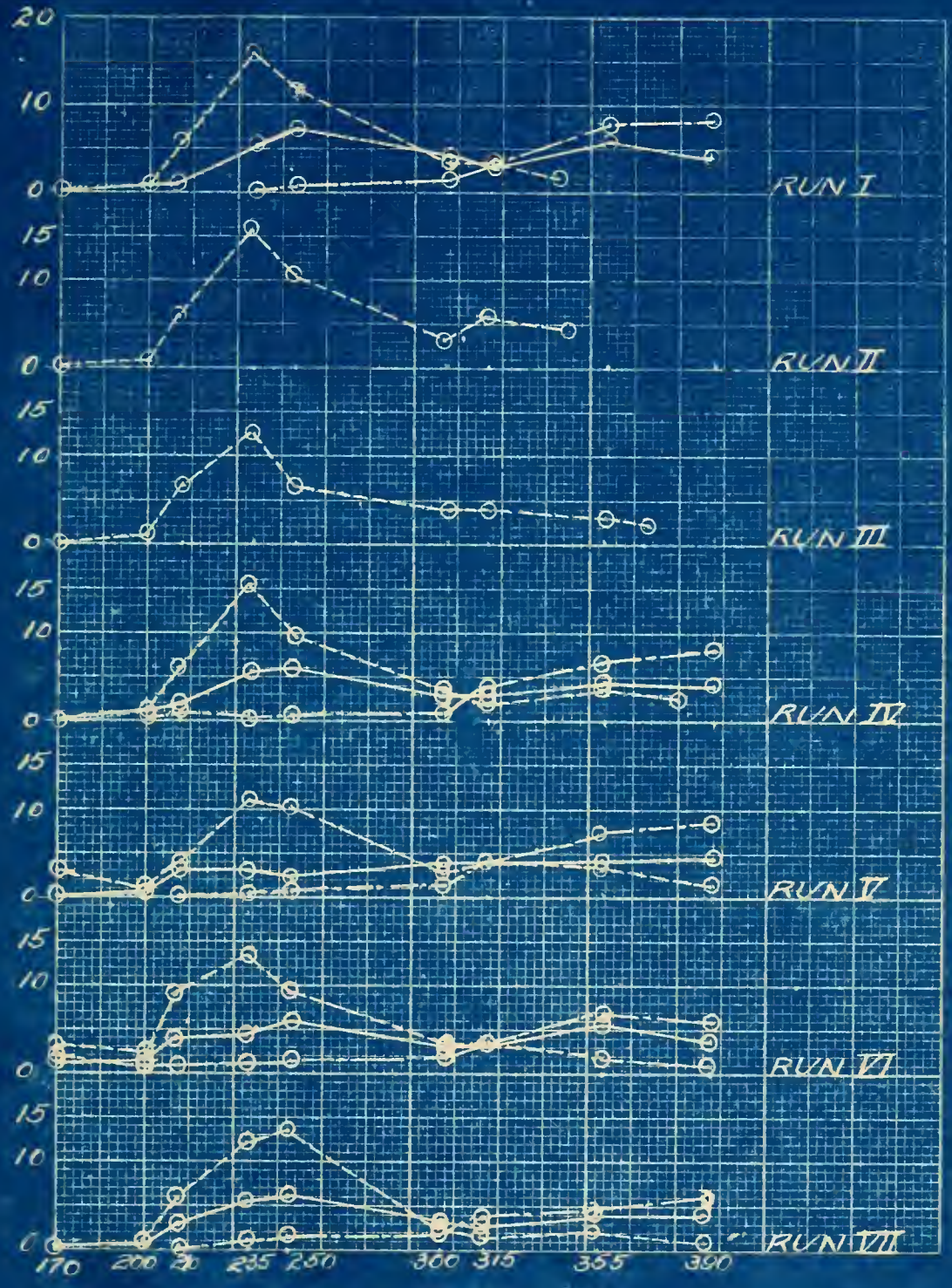
PER CENT OF DISTILLATE PER UNIT TEMPERATURE DIFFERENTIAL CURVES.

The bulb distillation results of the seven runs were used in the construction of this graph. The percentage obtained for each temperature differential were divided by the temperature differential and multiplied by ten and plotted on the y-axis of the graph. Temperatures of distillation were plotted on x-axis. For illustration Run 1, fraction A, bulb distillation is

TEMPERATURE DIFFERENTIAL		PER CENT OF OIL PER TEMPERATURE DIFFERENTIAL	PER CENT OF OIL PER UNIT TEMPERATURE DIFFERENTIAL.
170-1.5			
200-3.5	30	2.0	0.66
210-9.0	10	5.5	5.5
235-49.0	25	40.0	16.0
250-66.	15	17.0	11.3
300-84	50	18.0	3.6
315-89.5	15	5.5	3.7
340-95	25	5.5	2.20

These curves show where the greatest amount of oil is distilled per degree for each temperature differential. It further shows that the percentage distillation of fraction C is not an arithmetic mean of fraction A and B. The per-

centage distillation of a composite cannot therefore be foretold from the distillation of its components.



LEGEND: FRACTION A.----FRACTION B.—— FRACTION C.——

CONCLUSIONS:

1. The marked increase of anthracene salts when catalytic agents and hydrogen were used is to be especially noted. The reason is probably that polymerization has taken place in the "contact chamber".

2. From tests of oils, it is evident that the per cent distillation per temperature differential of the composite is not the arithmetic mean of its components. This leads to the conclusion that by a reasonable number of distillations, a Coal Tar product such as anthracene could not be concentrated to any high degree of purity.

3. Due to the deposition of carbon on the catalytic material and the presence of luminous gases coming off with the hydrogen one would be led to conclude that dehydrogenation has taken place to some extent.

4. If coal tar is to be hydrogenated commercially for the production of anthracene salts and increased oil yield per gal of tar, we would propose an intermittant operation with

a large "catalytic" area; operating half of the catalytic area for hydrogenation while the other half be flushed with an inert gas to replace the hydrogen and the hydrocarbons and the deposited carbon removed by combustion with air or pure oxygen.

5. The yield of naphthalene from the tar is not affected when the tar is distilled under vacuum or when the hydrogen and the vapors of distillation are passed over the catalytic agent in the contact chamber. The yield of naphthalene is decreased when distillation with hydrogen is made with aluminum chloride in tar. The decrease is largest when distillation is made with aluminum chloride in tar and passing the vapors of distillation and the hydrogen over reduced aluminum chloride in the contact chamber.

REFERENCES.

The methods of analysis used to obtain results in the table are those published by J.W. Weiss in The Journal of Industry and Engineering Chemistry, Vol. 10, No.9, pp. 732-738; Vol. 10, No.10, pp. 817-823; Vol. 10, No.11, pp. 911-916 and Vol. 10, No. 12, pp. 1006-1012.

OTHER REFERENCES:

"The Pyrogenesis of Hydrocarbons" Part 1, Historical and Bibliographical, By E. Lawson Lomax, Journal of Industrial and Engineering Chemistry, Vol. 9, No.9, pp. 879 to 902.